

**GENERAL  ELECTRIC
COMPANY**

**RE-ENTRY AND
ENVIRONMENTAL
SYSTEMS DIVISION**

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Dr. John Buckley
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Dear Dr. Buckley:

Enclosed are two (2) copies each of papers presented during
Session #2 of the "Welding, Bonding and Joining" Symposium.

Sincerely yours,

Ralph R. Hockridge

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/am

Enclosure

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1.0 INTRODUCTION

Most metallic, and non-metallic surfaces which are to be adhesively bonded are heavily contaminated with oxides, oils, shop soils, fingerprints, etc., and require some cleaning treatment prior to the bonding process. The importance of surface preparation and cleanliness cannot be over-emphasized, therefore, and many investigators have shown convincingly that the performance and durability of the adhesive bond is to a large extent governed by the thoroughness of surface preparation.

Surface contamination in the form of rust, scale, oil, grease, and dirt is usually obvious. Nearly invisible contamination, on the other hand, may also be present, and represents a much greater potential hazard for premature bond failure. Examples of the latter are soldering flux residuals, perspiration in the form of hand and finger marks, chlorides from marine atmospheres, and sulfates from industrial atmospheres. Greases and oils, which lead to poor bond adhesion, are generally easily noticed and removed from the surface. Oxide and oxide-promoting agents, on the other hand, are much more insidious, and the reactions leading to premature adhesive failure may not take place until the article has been in service for some time and exposed to a severe environment, for example, high humidity or water immersion.

2.0 ALUMINUM

Recognizing that contaminants on the surface to be bonded can result in premature failure, considerable emphasis has been placed in recent years in the techniques of surface preparation. For example, in the use of aluminum, techniques have varied from the original concepts of solvent wipe, or sand and solvent wipe, to vapor degreasing, to chemical treatments which provide complex chromates as a surface layer, to acid paste treatments, to the most commonly utilized method today, of a dichromate-sulfuric acid dip treatment.

However, in spite of the rather extensive data available from materials suppliers on adhesives as bonded to metallic surfaces, little information is generally available on the performance or bond strength of adhesively bonded joints when exposed to the weather. In Reference 1, it was stated: "It is commonly recognized that adhesive bonded joints are subject to deterioration under adverse environmental conditions. Weather can have a deleterious effect on the polymeric adhesive itself or on the adherend. In the latter case a weak surface layer is formed (as in corrosion) and the overall strength of the joint is reduced. The bond between the adherend and the metal itself may be seriously affected, especially if the joint is stressed during the time of exposure".

In the study referenced above, fourteen different adhesives were applied to 2024-T3 grade aluminum in the form of lapped bonded specimens which were exposed to the weather at Picatinny Arsenal, New Jersey; Yuma, Arizona; and the Panama Canal Zone; and also exposed to MIL-STD-304 temperature and humidity cycling test. A typical lap shear specimen generally utilized is shown in Figure 1, and represents the type utilized at GE-RESO. After a one year exposure at the Picatinny site, it was shown that the bonded joints prepared by sandblasting, as well as those joints prepared with the commercial acid paste treatment, showed a considerable loss in strength, while those joints prepared with sodium dichromate-sulfuric acid treatment showed greater retention of strength. It was concluded that the acid paste and sandblast treatments resulted in a surface more susceptible to humidity attack than did the acid-dip treated surface.

Other studies conducted on aluminum (2) have examined filiform corrosion on aircraft aluminum alloys, both clad and unclad, overcoated with various protective paint coatings.

Another recent investigation (3) was conducted to study corrosive delamination of test panels representative of typical aircraft construction. In particular, the relative corrosive performance of clad vs bare aluminum alloys was evaluated. Failures observed on clad alloys were considered to be the resultant of galvanic corrosion in the bond line due to differences in electro-chemical potential between the cladding and the base alloys. Table I lists the potential of some commercial aluminum alloys.

<u>ALLOY</u>	<u>TEMPER</u>	<u>POTENTIAL, VOLTS</u>
2024	T3	-0.68
2024	T81	-0.80
1230	---	-0.84
7075	T6	-0.81
7072	---	-0.96
5052	H34	-0.85

TABLE 1. ELECTRODE POTENTIAL OF SOME COMMERCIAL ALUMINUM ALLOYS (3)

Figure 2 shows the progressive pitting action observed in bare and clad alloys, and shows that pitting is less likely to take place on clad alloys, and where pits do form that penetrate to the base alloy, lateral growth is initiated. This lateral corrosion growth results in more severe degradation of the bonded interface than does the pit growth characteristic of the bare alloy, and initiates a bond delamination failure.

An investigation had been conducted in-house (4) to evaluate the effects of humidity on epoxy bonded lap joints exposed to an environment more severe than the MIL-A-5090 requirements. The exceptions to the environment are shown in Table 2.

<u>MIL-A-5090</u>	<u>TEST CONDITIONS</u>
120°F (322°K)	160°F (344.3°K)
Exposed area 2 lineal inches (50.8 mm)	Exposed area 3 lineal inches (76.2 mm)
Panel suspended vertically for drainage.	Panel laid flat to allow moisture condensation.

TABLE 2. TEST CONDITIONS (4)

The evaluation was conducted on 2024-T3 bare aluminum. Aluminum treatments prior to bonding included solvent degreasing for all panels with one set receiving a dichromate-sulfuric acid dip treatment, and the other set a commercial acid paste treatment. Lap shear ultimate strength data were obtained in the temperature range -75°F (213.7°K) to +400°F (477.6°K) prior to, and after a fourteen (14) day exposure to a relative humidity of 95 + 5 - 0%, and a temperature of 165 ± 5°F (347 ± 2.8°K) in an automatically controlled chamber. The data, shown in Figure 3, indicated that although an approximate 25% decrease in lap shear strength was realized as a result of the humidity exposure on the acid paste treated surface, no adhesive failures were noted and the degraded property values were adequate for the particular design. Although slightly higher in value, the acid dip values decreased in a similar manner, and as indicated above (1), the acid dip treated surface retained a greater percentage of

strength. Test specimens were of the configuration shown in Figure 1. It must be emphasized that this data was obtained on non-porous adherends. It will be shown that in the case of one non-porous and one porous adherend, the environmental degradation is more severe.

3.0 CORK - ALUMINUM

In the case of one porous adherend, the effects of humidity exposure may be considerably more severe as is evidenced by a recent bonding problem on an in-house project. An insulative material, reconstituted cork in a resin matrix in sheet form, is bonded in a brick pattern to the exterior surface of an aluminum conical shape as typified by Figure 4. A typical cross-section of the insulated structure is shown in Figure 5.

Preparation of the outer surface of the aluminum faced aluminum honeycomb structure included solvent cleaning, application of a commercial acid paste treatment, pressure rinsing with water until the drippings from the structure were neutral, and an air dry period.

The cork insulation, pre-cut (lofted) to size, was placed on the structure by placing the edge of the sheet in contact first, to sweep any air entrappment to the edge of the sheet. Prior to contact, each sheet received a thin, $\sim .005$ " (.13 mm) layer of an unfilled epoxy-polyamide adhesive, as did the faying surface of the aluminum. Each sheet, applied in a brick pattern, was taped to its adjoining sheet, and after completion of the lay-up, the entire assembly was vacuum-bagged and cured at an elevated temperature of 135°F (330.4°K) for four (4) hours at 29" Hg ($97.929 \times 10^3 \text{ N/M}^2$). Subsequently, as a portion of the required testing of an aerospace assembly, the cork insulated structure was exposed to a series of cumulative tests:

1. Three day cyclic humidity per Figure 6.
2. Seven day cyclic humidity per Figure 6.
3. A temperature/altitude test to expose the bonded assembly to rapid depressurization to one torr and 0°F (255.4°K), representative of an altitude and temperature of 150,000 feet (45.7 kilometer).

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Upon removal from the temperature/altitude chamber, large areas of unbond were observed at the edges of the cork "brick work", and also "bubbled" lifted areas in the centers of some of the cork insulative panels. Sectioning of the failure areas indicated the presence of a few pit areas such as shown in Figure 2A, but more importantly, gross delamination of the cork and entire epoxy bond system from the aluminum substrate. A second assembly was then tested with similar results, as were test panels especially prepared to evaluate the corrosive delamination problem. To determine whether the delamination was initiated by moisture permeation from the cork seams, or was moisture penetration through the cork, test assemblies were prepared in the normal fashion, except with all cork seams sealed with various generic sealers. It became quickly obvious that seam sealing offered no advantage, moisture permeation of the cork matrix was undoubtedly the culprit, and that the acid paste treated surface was more susceptible to delamination than an aluminum oxide paper sanded and solvent cleaned surface.

Test assemblies were then fabricated utilizing several primers, including standard adhesion promoting types, and several anti-corrosive primers. In all cases where the anti-corrosive types of primers were utilized, no lifting or delamination of the cork was observed, and in subsequent panel tear-downs, no corrosion was evident on the aluminum surface. Subsequently, an epoxy-polyamide primer was selected as the most compatible with the existing epoxy adhesive. The primer is green in color and contains strontium chromate pigment. The general application procedure is:

1. Solvent clean the aluminum with acetone or Methyl Ethyl Ketone (MEK).
2. Uniformly sand with 240 grit aluminum oxide paper.
3. Vacuum to remove sanding residue.
4. Solvent clean with acetone, followed by a low residual denatured alcohol.
5. Oven dry one (1) hour at 125°F (324.8°K).
6. Spray apply the epoxy primer to a dry film thickness of 0.002 inch (0.05 mm).
7. Air dry fifteen (15) minutes, and oven cure at 200°F (366.5°K) for two (2) hours.

Once primed, the assemblies may be stored at ambient conditions for periods up to six (6) months prior to cork insulation adhesive bonding. Prior to adhesive application and vacuum-bag bonding as described above, the primed assembly is:

1. Solvent cleaned with low residual denatured alcohol.
2. Uniformly sanded using 240 grit aluminum oxide paper to remove all surface gloss.
3. Vacuum cleaned to remove sanding residue.
4. Solvent cleaned with MEK and allowed to air dry for one (1) hour.

NOTE: Step 1 may be omitted if the primed assembly has not been stored after primer cure.

Since incorporation of the anti-corrosive primer into the bonding system, no humidity failures have been encountered on that assembly in a two (2) year manufacturing period.

4.0 CORK - TITANIUM

Mindful of the prior environmental problems associated with corrosive delamination, when a recent program required adhesive bonding of cork to titanium alloy 6-Aluminum -4 Vanadium, a test program was immediately established to verify the need for an anti-corrosive primer in the bond system.

Since the assembly precluded the use of dip treatments, or those requiring a rinse after treatment, panels nominally 12 inch x 12 inch x 0.060 inch (304.8 x 304.8 x 1.52 mm) were prepared as follows:

1. Solvent clean with MEK.
2. Sand with 240 grit aluminum oxide paper.
3. Solvent clean with MEK.

One-half of the test panels were then primed with the chromate/epoxy primer utilized for the aluminum bond efforts described above, and all panels were bonded with 0.25 inch (6.35 mm) cork utilizing a filled, flexibilized, epoxy-amine cured adhesive.

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After the cure, the panels were exposed to three (3) cycles of temperature-humidity per Figure 6 and inspected for unbonds. After inspection, the panels received seven (7) more cycles per Figure 6, and were again inspected. Upon conclusion of the ten cycles of temperature-humidity, the panels were exposed to a twelve (12) hour salt-fog test, and again inspected. The salt-fog conditions were as noted in Table 3.

CHAMBER CONDITIONING

16 Hours Prior to Test
95°F + 20° - 5° (308.2°K + 11.1 - 2.8)

TEST CONDITION

12 Hour Cycle
95°F + 2° - 4° (308.2°K + 1.1 - 2.3)
Salt Conc. = 3.6 ± 0.1%

TABLE 3. SALT FOG CONDITIONS

The test results are tabulated in Table 4 and show that only the panels primed with anti-corrosive primer can successfully pass the vehicle preflight test environment. Use of the anti-corrosive primer has, therefore, been incorporated into this system as pre-bond requirement.

5.0 SUMMARY

The use of an anti-corrosive primer has been shown to be essential to assure survival of a bonded structure in a hostile environment, particularly if a stress is to be applied to the adhesively bonded joint during the environmental exposure.

For example, the Lockheed L-1011 TriStar assembly, after exhaustive evaluation tests specifies use of chromate filled inhibitive polysulfide sealants, and use of corrosion inhibiting adhesive primers prior to structural bonding with film adhesive (5).

The day of corrosion-resistant primers is just beginning to dawn, and no bonded assembly subject to a humid environment should be designed without consideration of corrosive delamination, and its catastrophic effects.

REFERENCES:

1. "How Weathering and Aging Affect Bonded Aluminum", R. W. Wegman, W. M. Bodnar, E. S. Duda, and M. J. Bodnar, Adhesive Age, October 1967, pp 22-26.
2. "Filiform Corrosion of Aluminum", W. L. Slabaugh, W. DeJager, S. E. Hoover, and L. L. Hutchinson, Journal of Paint Technology, Vol. 44, No. 566, March 1972.
3. "Corrosive Delamination", Dr. F. J. Riel, SAMPE Journal, August/September 1971.
4. "Effect of Environmental Exposure on Bonded Aluminum Treated with Organic Conversion Coatings", R. R. Cerankowski, 10/5/64, Internal General Electric Document 8158-4004.
5. "L-1011 TriStar Places New Demands on Aircraft Sealants and Adhesives", D. A. Petrino, Adhesives Age, February 1972, pp 15 - 19.

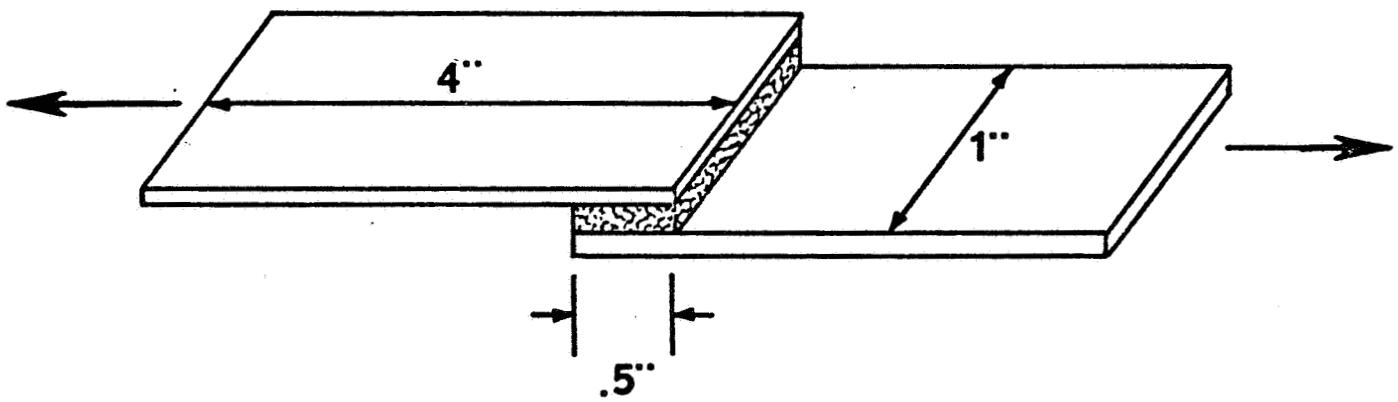


FIGURE 1

TYPICAL LAP SHEAR SPECIMEN

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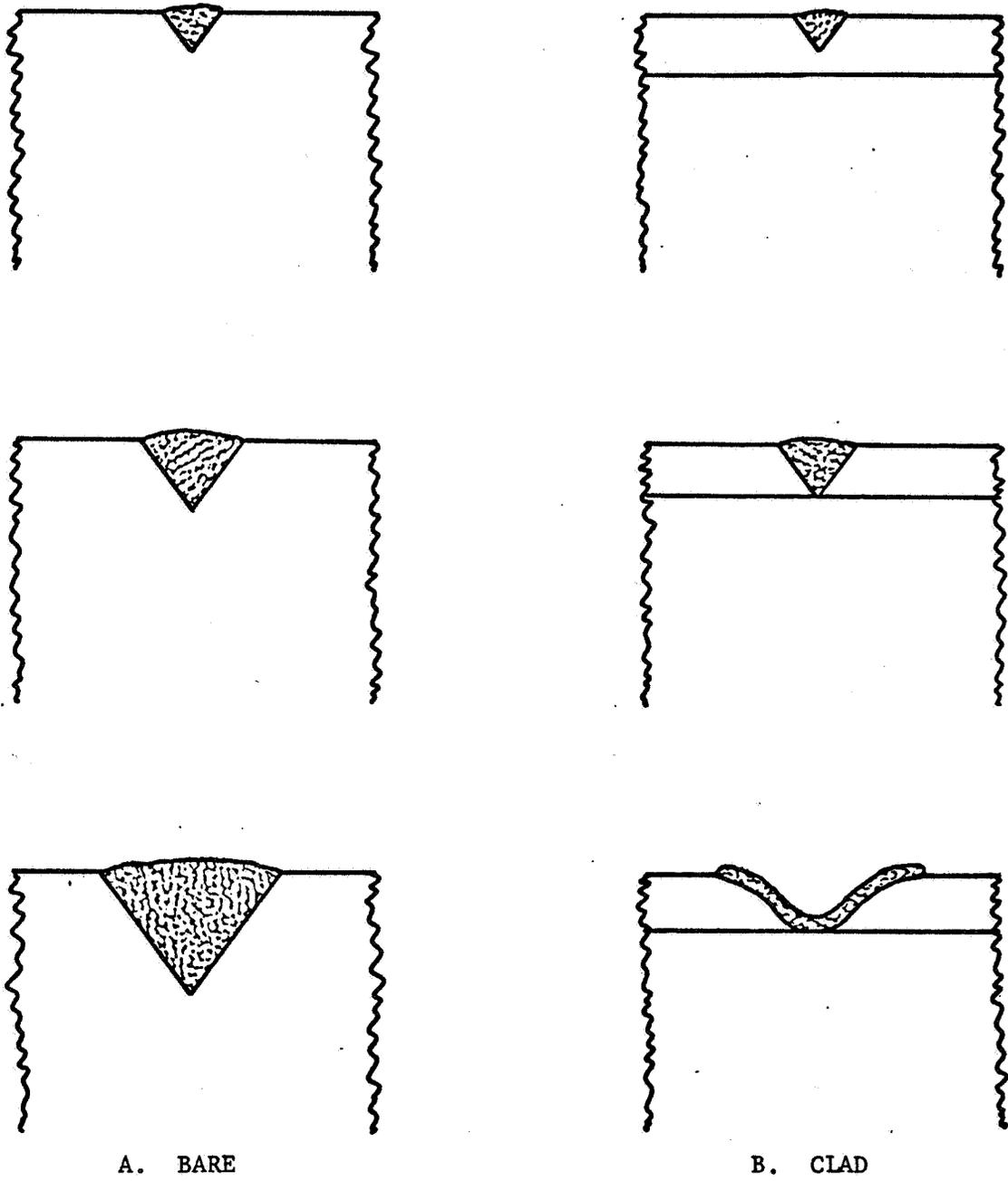


FIGURE 2.

PROGRESSIVE PITTING OF BARE AND
CLAD ALUMINUM IN A CORROSIVE ENVIRONMENT (3)

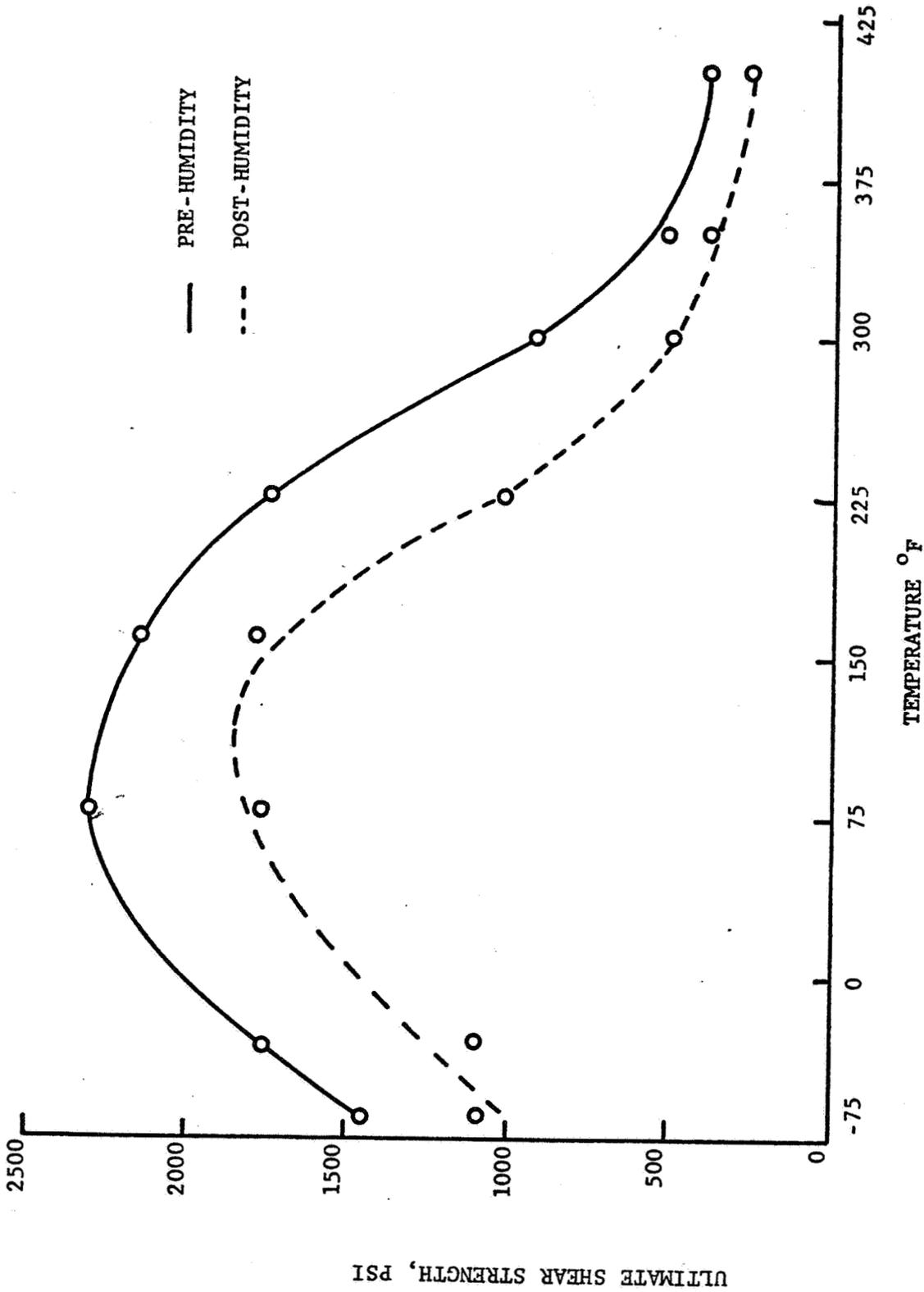


FIGURE 3

LAP SHEAR STRENGTH - HUMIDITY ENVIRONMENT

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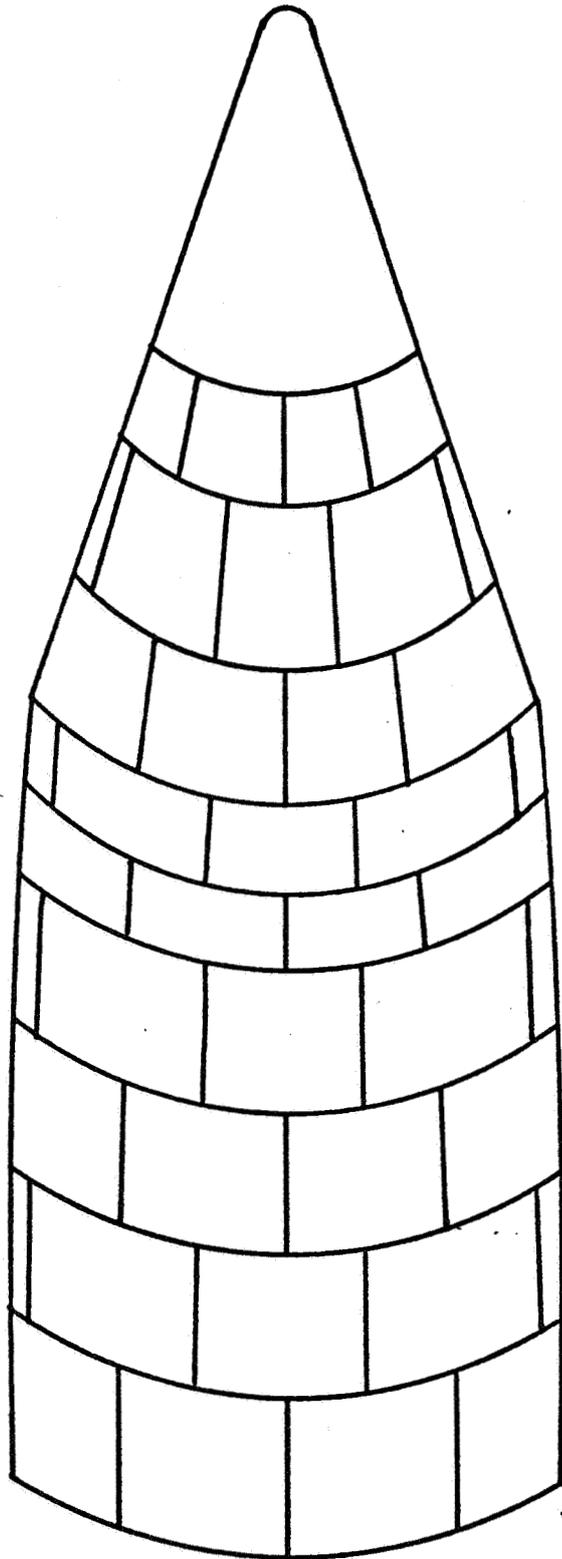


FIGURE 4

CORK INSULATED STRUCTURE

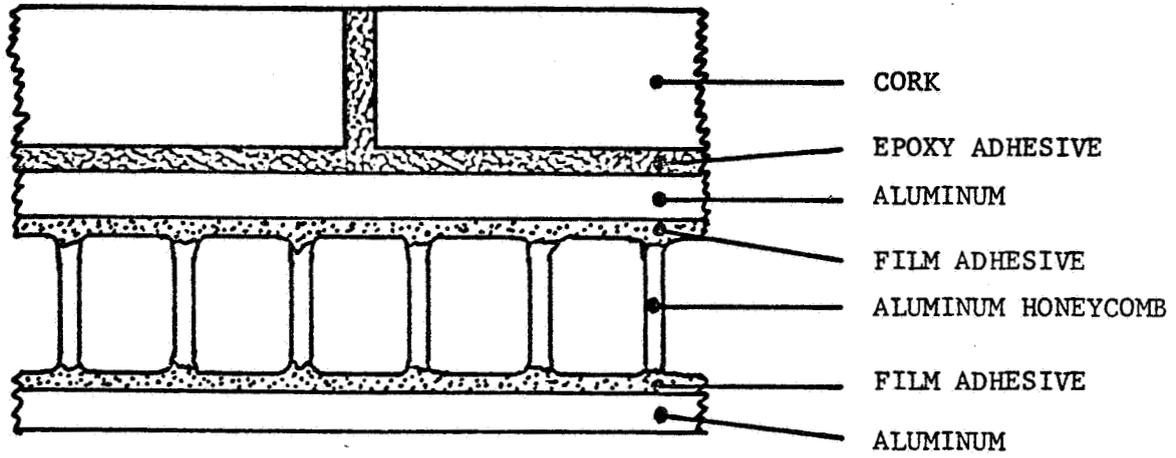


FIGURE 5

TYPICAL STRUCTURE CROSS-SECTION

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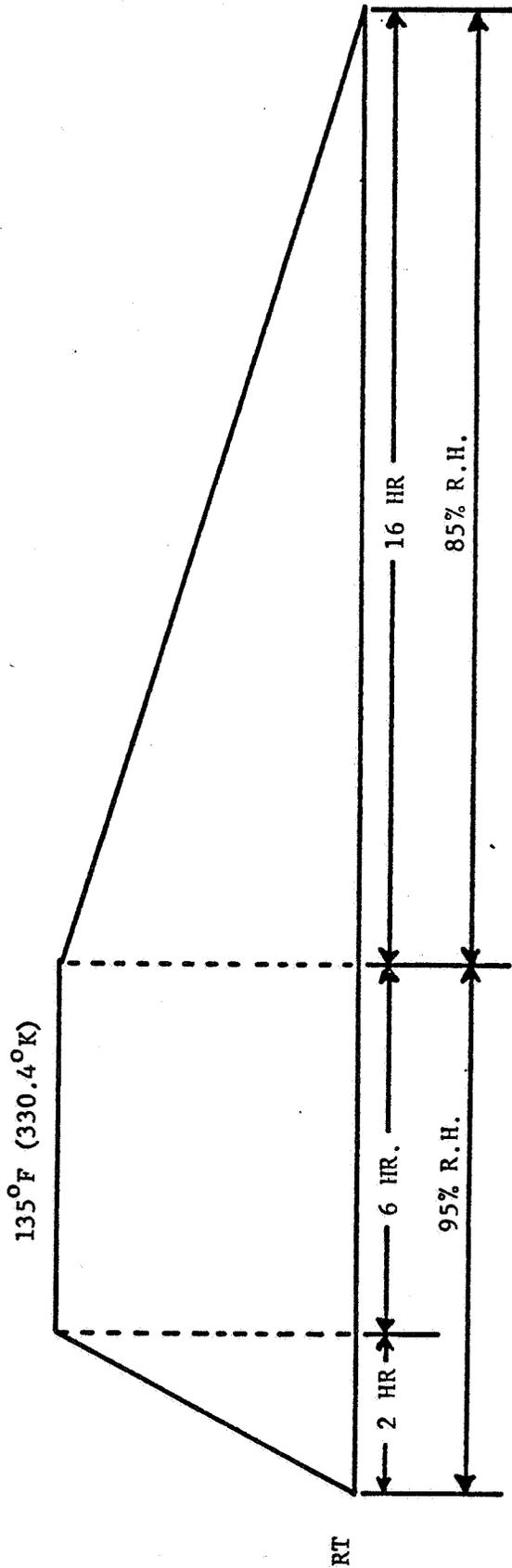


FIGURE 6

CYCLIC TEMPERATURE-HUMIDITY

TABLE 4

SUMMARY OF CORK-TITANIUM BONDED SPECIMENS IN ENVIRONMENTAL TESTING

<u>SPECIMEN NUMBER</u>	<u>TYPE</u>	<u>POST 3 DAY T/H EVALUATION</u>	<u>POST 10 DAY T/H EVALUATION</u>	<u>POST 10 DAY T/H + 12 HR S/F EVALUATION</u>
75	Unprimed	OK	----	----
76	↓	OK	Side A 1.1" Unbond 1.5-2.0" Unbond	----
			Side D 0.8" Unbond 2" Unbond	----
		OK	Side A 1.1" Unbond 1.0" Unbond 4-5" Unbond	Side A - open and unbonded most of way
77			Side B 0.4" Unbond 1.7" Unbond	Side B 2" Unbond ½" Additional Unbond
			Side C 3.9" Unbond 0.9" Unbond	Side C 4.5" Unbond 1.0" Unbond
				Side D 0.35" Unbond
78	Primed ↓	OK	----	----
79		OK	OK	----
80		OK	OK	OK